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(54) PURIFICATION OF SULFUR-CONTAINING WASTE GASES WITH HYDROGEN PEROXIDE

(71) We, FMC CORPORATION, a corporation incorporated in the State of Delaware, United States of America, of 633 Third Avenue, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the removal of sulfur-containing gases present in a waste gas stream before the gases are released into the atmosphere.

Sulfur-containing waste gases are noxious, often toxic, and are produced as by-products in many industrial operations. For example, sulfur-containing gases are present in effluent gas streams from flue gases, smelter gases, off-gases from chemical and petroleum processes, and stack gases produced from the combustion of sulfur-containing hydrocarbon fuels. These gases contain hydrogen sulfide, sulfur dioxide, aliphatic thiols, and organic sulfide compounds including sulfides, disulfides, polysulfides, and thiophenes and mixtures thereof. The term "organic sulfide compounds" refers to organic compounds containing a divalent sulfur atom which is not bonded to a hydrogen atom. Pollution of the environment by such gases has been offensive to communities surrounding the pollution source because of their noxious presence in the atmosphere and because of their harmful effect on natural habitat.

Many processes have been proposed for removing sulfur-containing gases from gaseous effluents. One of the earliest methods was the incineration method. In this method, toxic hydrogen sulfide and organic sulfides were converted to less toxic and less offensive sulfur dioxide and sulfur trioxide by air oxidation at high temperatures. While this process converted toxic substances into less toxic substances, the less toxic substances

were still noxious and potentially dangerous to the environment.

To avoid the problems associated with the incineration method, numerous chemical processes have been suggested, but there has been a long felt need for a commercially effective process capable of rapidly removing a multitude of different sulfur-containing gases present in a waste gas stream in a simple and convenient manner without the formation of by-product pollutants.

In accordance with the present invention there is provided a method of simultaneously absorbing and oxidizing a sulfur-containing gas present in a waste gas stream in which the sulfur-containing gas is sulfur dioxide, an aliphatic thiol containing 1 to 12 carbon atoms or a mixture of such gases, and possibly also contains hydrogen sulfide and/or one or more organic sulfides and/or thiophenes, that comprises contacting the waste gas stream with an aqueous hydrogen peroxide solution having a pH above 7.0 and a hydrogen peroxide concentration in the range 0.01 to 50 weight per cent at a temperature above the freezing point but below the boiling point of the solution for a sufficient time to simultaneously absorb and oxidize the sulfur-containing gas.

The invention permits of the removal of essentially all of the sulfur-containing gases present in a waste gas stream to below levels detectable by conventional equipment within a matter of a few seconds. Furthermore, the sulfur-containing gases are converted to non-polluting alkali metal sulfates and sulfonates. These substances may be discharged directly into natural waterways without harm to natural fauna or flora.

Among the aliphatic thiols (mercaptans) containing 1 to 12 carbon atoms are methanethiol, ethanethiol, propanethiol, and butanethiol. Among the organic sulfide compounds (including organic disulfides and polysulfides) are dimethyl sulfide, diethyl sul-

fide, dibutyl sulfide, methyl ethyl sulfide, dimethyl disulfide and diethyl disulfide. The thiophenes may be substituted or unsubstituted.

- 5 The oxidation rates of these organic sulfide compounds are not pH-dependent, and the compounds are absorbed and oxidized by the aqueous hydrogen peroxide solution to non-polluting compounds. Accordingly,
10 the other organic sulfide compounds are processed simultaneously with the other sulfur-containing gases, namely sulfur dioxide, C₁₋₁₂ aliphatic thiols, and possibly hydrogen sulfide, which are the principal sulfur-containing gases in most waste-gas streams, thus avoiding costly and difficult separation procedures and subsequent processing steps.

- 20 The concentrations of sulfur-containing gases that are treated can vary widely. Generally, the sulfur-containing gas concentration is source-dependent and varies from a few mg/l to several percent, such as 5% by weight. The process is most economical if
25 the sulfur-containing gas concentration in the waste gas stream is maintained at less than 2% by weight. By decreasing the sulfur-containing gas concentration to less than 2%, such as by diluting the gas with air, the quantity of hydrogen peroxide necessary to oxidize a unit quantity of the sulfur-containing gas is substantially reduced. Dilution with air prevents hydrogen sulfide gas mixtures from containing more than 4.3%
30 hydrogen sulfide, which mixtures are explosive.

- In order that the sulfur-containing gases should be simultaneously absorbed and oxidized by the aqueous hydrogen peroxide solution, the aqueous solution must have a pH above 7.0, and preferably not exceeding 13.5. The desired pH is obtained by adding an alkali to the aqueous hydrogen peroxide solution. The preferred alkali is sodium hydroxide which may be replaced in whole or in part by potassium hydroxide, magnesium hydroxide, calcium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate or magnesium carbonate. If the pH of the aqueous solution drops below 7.0 during the reaction, additional alkali is added to raise the pH of the solution above 7.0. Maintenance of the pH above 7.0 is essential in order to neutralize the sulfuric and sulfonic acids produced during the course of the reaction. This procedure prevents the need for subsequent pH adjustments prior to the discharge of the aqueous solution. Monitoring the pH of the reaction mixture is achieved conventionally.

- 60 The pH of the aqueous hydrogen peroxide solution may be further adjusted within the above pH ranges to achieve optimum absorption and oxidation of specific sulfur-

containing gases present in specific waste gas streams. For example, when the sulfur-containing waste gas contains hydrogen sulfide, the pH is preferably between 8.0 and 13.5, particularly between 11.0 and 13.0. Within the preferred pH range, hydrogen sulfide is rapidly absorbed and oxidized. Absorption and oxidation rates are significantly improved at the high pHs. When sulfur dioxide is the sulfur-containing waste gas, the pH is preferably in the range 7.0 to 12.0. In this pH range, the absorption rates are significantly improved. When the pH is above 12.0 the oxidation rate of sulfur dioxide is too slow for commercial operation. When C₁₋₁₂ aliphatic thiols are the sulfur-containing waste gas, the pH is preferably in the range 7.0 to 13.5. When the waste gas streams contain a mixture of the foregoing sulfur-containing gases, the absorption and oxidation rate of all of the sulfur-containing gases is optimal at the preferred pH range of 8.0 to 12.0. The oxidation rates of the organic sulfide compounds, are not pH dependent and consequently any pH above 7.0 may be used to oxidize these gases.

Any available grade of aqueous hydrogen peroxide can be used, with 50% technical grade being preferred. The exact quantity of hydrogen peroxide in the aqueous solution depends upon the concentration of the sulfur-containing gases present in the waste gas stream and the extent to which these gases are to be removed. The aqueous hydrogen peroxide solution can be prepared with deionized, distilled or tap water.

To reduce the sulfur-containing gas content present in a waste gas stream to non-detectable limits, hydrogen peroxide is used in concentrations of 0.01% to 50% by weight. The specific amount of hydrogen peroxide to be used to oxidize a specific sulfur-containing gas is easily determined from the stoichiometry of the reaction. For example, four moles of hydrogen peroxide are needed to completely oxidize one mole of hydrogen sulfide; one mole of hydrogen peroxide is needed to completely oxidize one mole of sulfur dioxide. However, amounts of hydrogen peroxide slightly above the stoichiometric amount may be used to oxidize either hydrogen sulfide or sulfur dioxide. The gaseous organic sulfur compounds require an excess of hydrogen peroxide over the stoichiometric amount with a maximum concentration of 10% hydrogen peroxide being preferred. The term "gaseous organic sulfur compounds" refers to both the aliphatic thiols and the organic sulfide compounds.

The use of hydrogen peroxide under alkaline conditions to simultaneously absorb and oxidize sulfur-containing waste gases is completely unexpected because hydrogen per-

oxide decomposes under alkaline conditions. It has been discovered, however, that the oxidation rate of hydrogen sulfide and sulfur dioxide is significantly faster than the hydrogen peroxide decomposition rate when hydrogen peroxide is used in stoichiometric amounts or in amounts slightly above the stoichiometric amount. It has also been discovered that hydrogen peroxide decomposition is kept to a nominal extent when oxidizing any of the gaseous organic sulfur compounds even when greater than stoichiometric amounts of hydrogen peroxide are used, by maintaining the pH of the solution in the range 7.0 to 12.0.

The time necessary to contact the sulfur-containing waste gas must be sufficient to simultaneously absorb and oxidize the sulfur-containing gases. Contact times of 1 second or less are sufficient to completely absorb and oxidize hydrogen sulfide and sulfur dioxide. Longer contact times are necessary to absorb and oxidize the gaseous organic sulfur compounds. These times range from 1 to 60 seconds depending upon the specific gaseous organic sulfur compound. To limit hydrogen peroxide decomposition during the longer contact times, the aqueous hydrogen peroxide solution may optionally be stabilized by conventional methods, such as by use of magnesium oxide or other stabilizers in the aqueous hydrogen peroxide solution. Likewise, a conventional metal catalyst may also be used to assist in the oxidation reaction. These catalyst include salts of iron, cobalt, nickel, copper, manganese, molybdenum, vanadium, platinum, palladium and silver. If a catalyst is used, the first four catalytic salts are preferred. The catalysts can be used with or without conventional complexing agents such as gluconic acid and citric acid. Hydrogen peroxide stabilizers and metal catalysts may also be used during the absorption and oxidation of hydrogen sulfide and sulfur dioxide even though they are not necessary for the reaction.

The reaction temperature is critical only to the extent that it must be above the freezing point but below the boiling point of the aqueous solution. The reaction is preferably carried out between 25° and 85°C, particularly between 45° and 65°C, which are the normal temperatures of waste gas streams. When oxidizing any of the gaseous organic sulfur compounds, temperatures between 60° and 70°C are preferred. At these temperatures, the gaseous organic sulfur compounds are rapidly oxidized at substantially increased rates. This rapid oxidation permits the use of only stoichiometric amounts of hydrogen peroxide instead of requiring excess hydrogen peroxide to completely oxidize all of the gaseous organic sulfur compounds present in the waste gas stream.

The waste gas stream is contacted with the

aqueous hydrogen peroxide solution in any conventional contacting device. The preferred contacting device is a packed column such as a packed bed or tower. The waste gas stream and contacting solution may be fed into the contactor either counter-currently, cross-currently or co-currently. The treated waste gas and spent aqueous hydrogen peroxide solution are then discharged directly into the environment.

When contacting waste gases which require only stoichiometric amounts of hydrogen peroxide to oxidize the sulfur-containing gases, it is preferred to pass the waste gas stream and aqueous hydrogen peroxide solution through the contactor only once. When contacting waste gases which require an excess of hydrogen peroxide over the stoichiometric amount, it is preferred to pass the waste gas stream and aqueous hydrogen peroxide solution through the contactor, separate the spent aqueous solution, and re-activate the spent aqueous solution by adding fresh hydrogen peroxide to the solution. This reactivated solution is then recycled to the contactor. By this procedure, excess of hydrogen peroxide is continuously provided in the contactor in an efficient and economic way.

Commercially available gas analysers are used to analyse the sulfur-containing gas content present in both the waste gas stream and in the effluent gas stream. If the sulfur-containing-gas concentration in the waste gas stream changes, the required amount of aqueous hydrogen peroxide solution added to the contactor can be added either manually or automatically. Furthermore, the pH of the spent aqueous hydrogen peroxide solution removed from the contactor is analysed by conventional means in order to keep the pH of the aqueous hydrogen peroxide solution during the reaction above 7.0. It has been found that if the pH of the aqueous hydrogen peroxide solution fed into the contactor is between 8.0 and 12.0, the pH of the removed aqueous solution will be above 7.0.

The following examples further illustrate the invention. All percentages given are based upon weight unless otherwise indicated and the words "Pyrex" and "Intalox" are trade marks.

EXAMPLE 1

A gas stream containing 0.1% SO₂ by volume in air was passed at a velocity of 56 cm/sec through a contactor consisting of a 5.08 cm (2-inch) diameter heat-and-chemically-resistant glass (Pyrex) pipe containing a 35.56 cm (14-inch) column of 0.63 cm (¼-inch) chemically resistant ceramic packing (Intalox saddles). The total gas flow was 50 l/min. An aqueous solution containing 0.2 g/l of NaOH and 0.16 g/l of H₂O₂ having

a pH of 11.2 was prepared with deionized water and passed through the column counter-current to the gas flow at a solution flow rate of 0.45 l/min. The temperature of the aqueous solution was 25°C. The residence time of the gas stream in the contactor was 0.66 seconds. The process was carried out continuously for one hour. The effluent gas stream contained less than 1 ppm SO₂. The effluent liquid had a pH of 9.0 and contained 1 mg/l sulfite values (Na₂SO₃, NaHSO₃).

EXAMPLE 2

A gas stream containing 1000 ppm methanethiol by volume in air was passed at a velocity of approximately 35 cm/sec through a contactor consisting of a 5.08 cm (2 inch) diameter Pyrex pipe containing a 71.12 cm (28 inch) column of 0.63 cm ($\frac{1}{4}$ inch) Intalox saddles. The total gas flow was 15 l/min. An aqueous solution containing 1.0 g/l NaOH and 1.0 g/l H₂O₂ having a pH of 11.9 was prepared with deionized water and passed through the column counter-current to the gas flow at a solution flow rate of 1.35 l/min. The temperature of the aqueous solution was 25°C. The residence time of the gas stream in the contactor was 4.4 sec. The process was carried out continuously for one hour. The effluent gas stream contained 4 ppm methanethiol. The effluent solution had a pH of 11.0 and the content of unoxidized sulfur compounds was below detectable limits.

EXAMPLE 3

The procedure of Example 2 was repeated except that the gas stream contained 8000 ppm H₂S by volume and 200 ppm methanethiol by volume in air. The effluent gas stream contained no detectable H₂S and 2 ppm methanethiol by volume. The effluent solution had a pH of 11.2 and the content of unoxidized sulfur compounds was below detectable limits.

EXAMPLE 4

The procedure of Example 2 was repeated except that the gas stream containing 1000 ppm ethanethiol by volume, 1000 ppm dimethyl-sulfide by volume, and 1000 ppm thiophene. The effluent gas stream contained no detectable sulfur compounds. The effluent solution had a pH of 11.9 and contained approximately 5 mg/l diethyldisulfide.

WHAT WE CLAIM IS:—

1. A method of simultaneously absorbing and oxidizing a sulfur-containing gas present in a waste gas stream in which the

sulfur-containing gas is sulfur dioxide, an aliphatic thiol containing 1 to 12 carbon atoms or a mixture of such gases, and possibly also contains hydrogen sulfide and/or one or more organic sulfides and/or thiophenes, that comprises contacting the waste gas stream with an aqueous hydrogen peroxide solution having a pH above 7.0 and a hydrogen peroxide concentration in the range 0.01 to 50 weight per cent at a temperature above the freezing point but below the boiling point of the solution for a sufficient time to simultaneously absorb and oxidize the sulfur-containing gas.

2. A method as claimed in Claim 1, in which the pH of the solution does not exceed 13.5.

3. A method as claimed in Claim 2, in which the sulfur-containing waste gas contains hydrogen sulfide and the aqueous hydrogen peroxide solution has a pH between 8.0 and 13.5.

4. A method as claimed in Claim 3, in which the aqueous hydrogen peroxide solution has a pH between 11.0 and 13.0.

5. A method as claimed in Claim 2, in which sulfur dioxide is the sulfur-containing waste gas and the aqueous hydrogen peroxide solution has a pH not exceeding 12.0.

6. A method as claimed in Claim 2, in which the sulfur-containing waste gas is an aliphatic thiol containing 1 to 12 carbon atoms.

7. A method as claimed in any preceding claim, in which the temperature of the aqueous solution is between 25 and 85°C.

8. A method as claimed in Claim 7, in which the temperature of the aqueous solution is between 45° and 65°C.

9. A method as claimed in Claim 1, 2 or 6, in which the aliphatic thiols are methanethiol, ethanethiol, propanethiol, and/or butanethiol.

10. A method as claimed in any preceding claim, in which the waste gas stream contains organic sulfides, organic disulfides, organic polysulfides, and/or thiophenes.

11. A method as claimed in any preceding claim, in which the pH of the solution is maintained in the desired range by addition of a sufficient amount of alkali.

12. A method as claimed in Claim 1 substantially as hereinbefore described in any one of the Examples.

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